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TITLE

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AN ANALYSIS OF THE EFFECT OF SYSTEM VARIABLES ON THE QUALITY OF THIN FILMS AND POWDERS PRODUCED BY LASER-BREAKDOWN CHEMICAL VAPOR DEPOSITION

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ABSTRACT

A gas phase process for large area depositions on an ambient temperature substrate using laser-induced dielectric breakdown of gas phase precursors has recently been developed.[1] Deposits of nickel alloys show excellent grain refinement (<10 nm) and metastable phase incorporation due to rapid quenching from the gas phase. Particle size distribution and compositional variance within the deposited films have been studied using electron microscopy and electron diffraction. Kinetic expressions to explain homogeneous gas phase nucleation and growth of the deposited materials have been developed in an effort to better understand this process. The effect of system variables on film and powder grain sizes has been studied. This analysis gives insight into the fluid flow/heat transfer patterns involved in the system and their effect on the final deposited material. Heat transfer and fluid flow patterns must be optimized to minimize residence time in the gas phase to prevent excessive agglomeration of the fine particles. Results of the effect of system pressure, gas phase composition, laser pulse energy, and gas flow rate will be presented as they effect particle size distribution within the deposition.

INTRODUCTION

The production of metal or metal oxide/carbide ultrafine particles on the order of 1 to 10 nm in the form of a powders offer excellent possibilities in the synthesis of new catalysts, solar collectors, electronic devices, as well as many other applications. Materials fabricated from these ultrafine particles (on the order of nanometers) may possess different physical and chemical properties than bulk materials such as; higher mechanical strengths and lower melting points, due to their very high grain boundary to volume ratio.[2,3]

At the present time considerable effort is being expended to produce ultrafine particles by a number of different conventional processes. Examples include; reaction and subsequent precipitation from a liquid solution[4], and the evaporation and decomposition of metal hydroxides to produce fine metal oxides.[5] Additionally, continuous films and ultrafine powders have been produced by laser breakdown chemical vapor deposition.[1] In this process a metal bearing vapor species {$Ni(CO)_4$, $Fe(CO)_5$, WF_6/H_2} is decomposed in a plasma generated by dielectric breakdown of an argon carrier gas. The process differs from the previously mentioned methods in that very short times (on the order of microseconds) at high temperatures are used as supported by the presence of Ni with metastable Ni_3C.[6] A study of argon plasma temperatures as a function of time by Radziemski et.al [7], indicate temperatures in excess of 10^4 °K.

Okuyama et. al.[5] studied particle nucleation and ultimate particle size. However in their study particle growth times in the gas phase were significantly longer (on the order of seconds), rather than on the order milliseconds as seen in the present study. These time differences result from their use of a continuous heat source, as compared to the pulsed heat source used in the present study. This leads to an increased effect of particle agglomeration in the Okuyama et. al. system. Particle size is a function of nucleus size, growth rate, and time available for growth of the particle via gas phase reaction.

EXPERIMENTAL

A schematic diagram of the system used to prepare the samples examined in this study is

shown in Figure 1. The energy input in this system is very localized, so that upon nucleation the fine particles have little time for growth before being deposited on the surface.

The standard operating conditions used consisted of a total system pressure of 10 Torr with a gas mixture of 1% $Ni(CO)_4$ and 99% Argon flowing at 200 cc/min (STP) and energy supplied by a pulsed laser operating at 1 Hz with an energy of 0.8 Joules per pulse. A plasma with a lifetime of 50-100 nsec is generated with the input of a 0.5 to 1.3 joule/laser pulse. The individual system variables were then adjusted to see the effect of each on the deposition thickness under the front of the plasma, the total surface area coverage, and finally the particle size as observed by electron microscopy.

In this study Ni/Ni_3C powders were produced, but Tungsten and Iron films have also been produced using this experimental system.[8] The samples were deposited directly on amorphous carbon films supported by copper grids to facilitate transmission electron microscopy (TEM). Previously, samples were also deposited on NaCl substrates and subsequently floated onto the TEM grids with no apparent change in microstructure in the prepared samples.[6] The microstructure of the films was determined using a Phillips 400T Electron Microscope operating at 100 KV. The microstructure produced by this process is very uniform and composed of grains on the order of 10 nm.[6] Observations using darkfield TEM indicate the minimum diffracting domain is on the order of 2.5 to 6 nm. This minimum diffracting grain size gives insight into the mechanisms of grain growth and heat transfer in the system and will be more fully discussed in the following section.

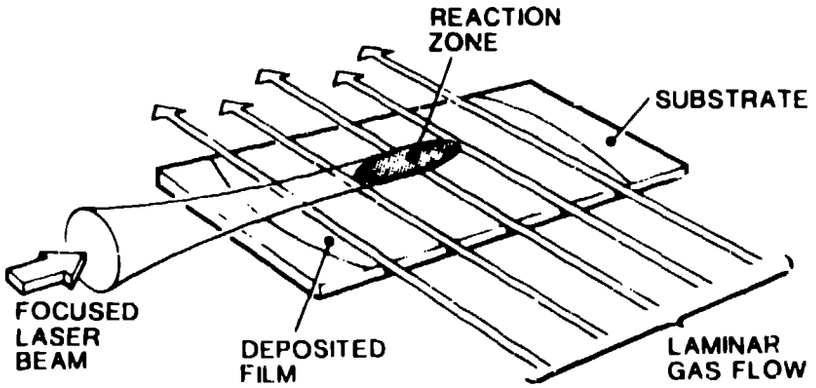

Figure 1: Schematic of experimental system.

ANALYSIS OF RESULTS AND DISCUSSION

In attempting to understand the mechanisms involved in both particle size development and also heat transfer in the system, one must first realize, that the heating within the system is very localized and that only a limited time for particle growth and contact with the flowing fluid is available. Since gas supply velocities as low as 300 cm/min effect the symmetry of the deposition, particle residence times in the gas phase must be on the order of milliseconds. The temperature of the plasma is initially very high ($>10^4$ K) though it comes to thermal equilibrium rapidly (<50 microseconds)[7]. The importance of this is only in regard to the species formed on dissociation of the metal precursor gas. Thermodynamic calculations show that at the temperatures of interest in the system , i.e. when condensation is occurring, the only stable species present are carbon monoxide, argon, and nickel in the molecular and elemental form. We have used a model based on homogeneous nucleation and growth[9-11] to explain condensation and have explained heat transfer by conduction from an instaneous line source.[12]

The critical nucleus size as determined from the Thompson Equation[13] was taken to be the size when the nucleation rate was approximately 10^{11} nuclei/cm^3 sec[10]. This resulted in critical nucleus sizes of approximately 0.2 nm. Growth rates were approximated using kinetic theory for growth in a multicomponent gas.[10] This results in a first order reaction in terms of $Ni(CO)_4$ partial pressure. The estimated critical nucleus size was subtracted from the observed minimum diffracting domain size and using a temperature averaged growth rate, the growth

time was determined. The growth time is shown in, Figure 2.

The cooling time was estimated as the time necessary to cool from the prescribed nucleation temperature (this varied from approximately 1000 to 1400°K) to room temperature using a time averaged cooling rate. The cooling time is also shown in Figure 2. The cooling rate was estimated using the initial temperature in the hot gas (based on the thermal properties of Argon only) to be at the dew point (saturation temperature of the nickel bearing gas), and using the derivative with respect to time of the solution to the temperature distribution for an instaneous line heat source.[12] The cylindrical surface area was used as a weighting factor for the positional cooling rate.

Examination of Figure 2 shows fairly good agreement between the cooling times and the necessary growth times. In both cases one can see a strong pressure dependency on both cooling and particle growth. These times correspond to cooling rates on the order of 10^5 to 10^6 °K/sec and residence times in the gas phase on the order of milliseconds. These cooling rates explain the existence of metastable Ni - supersaturated with carbon and Ni_3C in the product powders and films[6].

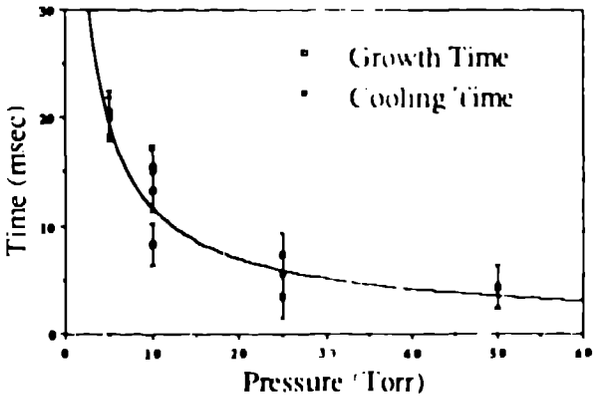

Figure 2: A comparison of calculated cooling and growth times as a function of system pressure

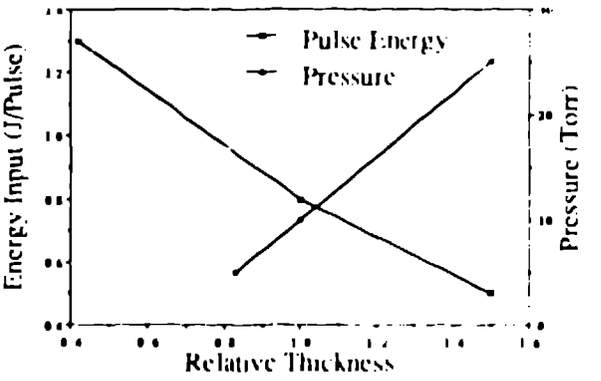

Figure 3: The effect of energy input and system pressure on deposition thickness.

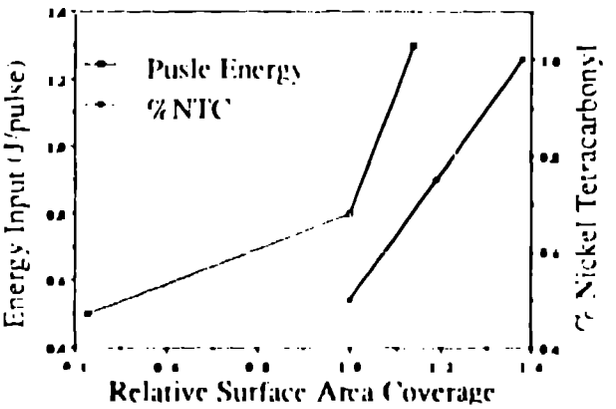

Figure 4: The effect of energy input and $Ni(CO)_4$ pressure on surface area coverage.

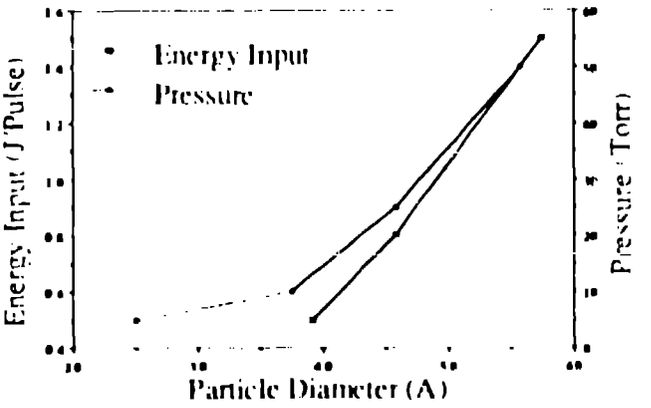

Figure 5: The effect of energy input and system pressure on particle diameter.

The most significant effects of system variables on the thickness of the deposition, area of coverage, and minimum diffracting domain (grain size) are shown in Figures 3 to 5. The results shown in Figure 3 indicate a higher local deposition with increasing pressure and decreasing energy input. Examination of Figure 4 indicates that the area of the deposition increases with increasing $Ni(CO)_4$ pressures and with higher energy inputs. Increasing energy input and total system pressure are seen to increase particle size, see Figure 5. In examining

the results of Figures 3 through 5, it becomes clear that higher energy inputs tend to increase both the deposition area and particle size. this is likely due to higher temperatures acting over a greater distance through the diffusion length, the result of a higher energy input. Additionally, as one would suspect, increasing the $Ni(CO)_4$ partial pressure increases the saturation ratio of the gas, leading to larger surface area coverage. The effect of either increased system pressure or partial pressure of $Ni(CO)_4$ indicates that the condensation reaction is a function of pressure. This agrees with the previous observations in terms of time dependency on growth and also cooling.

CONCLUSIONS

The results of this study indicate that nanocrystalline materials of a consistent size (2.5 to 6 nm) can be made using laser breakdown chemical vapor deposition. Additionally, analysis of the system employing gas phase condensation by homogeneous nucleation and growth, coupled with heat transfer by conduction explains the observed grain sizes and metastable phases formed.

ACKNOWLEDGEMENTS

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